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THE TUNGSTEN-TO-TUNGSTEN TRIPLE BOND. 7. REPLACEMENT OF DIMETHY--ETC(U)
MAY 77 M AKIYAMA, M H CHISHOLM, F A COTTON N00014-76-C-0826
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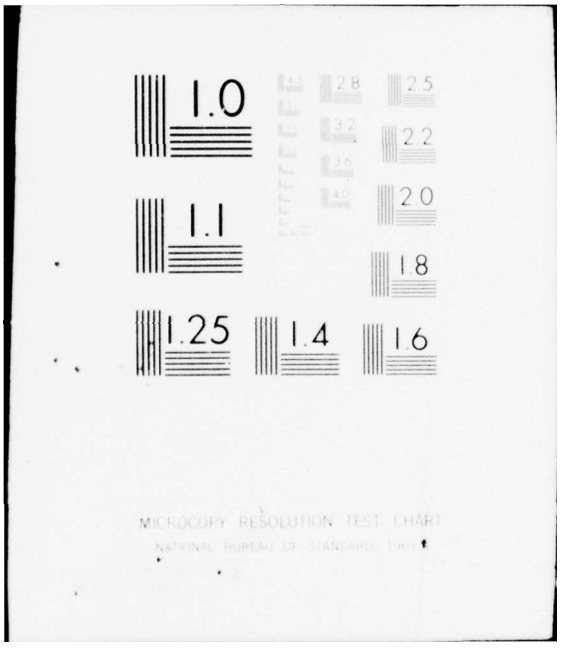
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$M_2(NMe_2)_6$ compounds (M = Mo,W) react with Me_3SiCl (2 equiv) in hydrocarbon solvents to give $M_2Cl_2(NMe_2)_4$ and Me_3SiNMe_2. An amine catalyzed reaction sequence is proposed: (1) $HNMe_2 + Me_3SiCl \rightarrow Me_3SiNMe_2 + HCl$ (ii) $M\text{-}NMe_2 + HCl \rightarrow M\text{-}Cl + HNMe_2$. This sequence is supported by the observations that $W_2(NMe_2)_6$ does not react with Me_3SiCl in the absence of amine and that

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20. (cont.) $W_2Cl_2(NMe_2)_4$ reacts rapidly with $HN(CD_3)_2$ to give $W_2(NMe_2)_6$ with complete scrambling of dimethylamine-d_0/d_6. In solution $W_2Cl_2(NMe_2)_6$ and $W_2(NMe_2)_6$ exist in equilibrium with $W_2Cl(NMe_2)_5$ ($K \approx 1$ at 30^0C). The compounds $M_2Cl_2(NMe_2)_4$ have been characterized by variable temperature ^1H nmr studies, infrared and mass spectroscopy and single crystal X-ray crystallography. The crystallographic data for $W_2Cl_2(NMe_2)_4$ are space group $P2_1/c$, $a = 15.061(8)$Å, $b = 13.338(7)$Å, $c = 8.372(3)$Å, $\beta = 96.68(3)^0$, $V = 1670(1)$Å^3, and $Z = 4$. $Mo_2Cl_2(NMe_2)_4$ is isostructural with the tungsten analog with $a = 15.031(2)$Å, $b = 13.146(1)$Å, $c = 8.411(2)$Å, $\beta = 96.36(1)^0$, and $V = 1664.3(3)$Å.^{3} In both molecules the $M_2N_4Cl_2$ moieties belong to the symmetry group C_{2h}. The M-M distances are 2.201(2)Å (M = Mo) and 2.285(2)Å (M = W).

The Tungsten-to-Tungsten Triple Bond. 7. Replacement of Dimethylamido by Chloro Groups In Hexakis(dimethylamido)ditungsten and -dimolybdenum Compounds; the Preparation, Properties and Structure of Dichlorotetrakis-(dimethylamido)ditungsten and -dimolybdenum.[1]

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Abstract

$M_2(NMe_2)_6$ compounds (M = Mo,W) react with Me_3SiCl (2 equiv) in hydrocarbon solvents to give $M_2Cl_2(NMe_2)_4$ and Me_3SiNMe_2. An amine catalyzed reaction sequence is proposed: (i) $HNMe_2$ + $Me_3SiCl \rightleftarrows Me_3SiNMe_2$ + HCl (ii) M-NMe_2 + HCl $\rightleftarrows$ M-Cl + $HNMe_2$. This sequence is supported by the observations that $W_2(NMe_2)_6$ does not react with Me_3SiCl in the absence of amine and that $W_2Cl_2(NMe_2)_4$ reacts rapidly with $HN(CD_3)_2$ to give $W_2(NMe_2)_6$ with complete scrambling of dimethylamine-d_0/d_6. In solution $W_2Cl_2(NMe_2)_6$ and $W_2(NMe_2)_6$ exist in equilibrium with $W_2Cl(NMe_2)_5$ ($K \sim 1$ at 30°C). The compounds $M_2Cl_2(NMe_2)_4$ have been characterized by variable temperature ^1H nmr studies, infrared and mass spectroscopy and single crystal X-ray crystallography. The crystallographic data for $W_2Cl_2(NMe_2)_4$ are space group $P2_1/c$, a = 15.061(8)Å, b = 13.338(7)Å, c = 8.372(3)Å, β = 96.68(3)°, V = 1670(1)Å^3, and Z = 4. $Mo_2Cl_2(NMe_2)_4$ is isostructural with the tungsten analog with a = 15.031(2)Å, b = 13.246(1)Å, c = 8.411(2)Å, β = 96.36(1)°, and V = 1664.3(3)Å.[3] In both molecules the $M_2N_4Cl_2$ moieties belong to the symmetry group C_{2h}. The M-M distances are 2.201(2) Å (M = Mo) and 2.285(2)Å (M = W).

Introduction

Prior work in our laboratories has established the existence of a structurally related series of compounds containing metal-to-metal triple bonds unsupported by bridging ligands: M_2L_6, where M = Mo and W, and L = R(alkyl),[3-5] NR_2[6,7] and OR.[8-10] It is our contention that these are merely members of a more general class of compounds of general formula $M_2X_{6-n}Y_n$, where M = Mo or W and X and Y are univalent ligands. The compounds $W_2X_2(NEt_2)_4$, where X = Cl,[11] Br,[12] I,[12] Me[13] and CH_2SiMe_3,[12] and $W_2Me_2(O_2CNEt_2)_4$[1,14] have been prepared and characterized; these compounds arose from our initial fortuitous isolation of $W_2Cl_2(NEt_2)_4$ from the reaction between WCl_4 and $LiNEt_2$.[11] In view of the lability of M-Cl and M-NR_2[15] groups toward a wide variety of metathetic and insertion (M-NR_2) reactions we sought synthetic routes to $M_2Cl_x(NR_2)_{6-x}$ compounds. In this paper we describe our studies of the reaction between $M_2(NMe_2)_6$ compounds and Me_3SiCl and our isolation and structural characterization of the new compounds $M_2Cl_2(NMe_2)_4$, where M = Mo and W.

Results and Discussion

Syntheses

From the reaction between WCl_4 and $LiNR_2$ (4 equiv) the dinuclear compounds $W_2(NR_2)_6$ were isolated[7] (NR_2 = NMe_2, NMeEt, NEt_2). Reactions employing $LiNEt_2$ (3 equiv) yielded[11] the red crystalline compound $W_2Cl_2(NEt_2)_4$ in low yield (10-20% based on tungsten). However, analogous reactions involving either $MoCl_3$ or other dialkylamidolithium reagents failed to yield $M_2Cl_2(NR_2)_4$ compounds: $M_2(NR_2)_6$ compounds were isolated. We supposed that $M_2Cl_x(NMe_2)_{6-x}$ compounds might be accessible starting from $M_2(NMe_2)_6$ compounds which themselves could be prepared in high yields.

$W_2(NMe_2)_6$ + Anhydrous HCl. Initially we reacted hydrocarbon solutions of $W_2(NMe_2)_6$ with anhydrous HCl. Even at low temperatures (-78°C) when HCl (1-2 equiv) was added by cautious vacuum line techniques an apparently diffusion controlled reaction occurred leading to the formation of a pink insoluble powder. ^1H nmr spectra showed that the hydrocarbon solutions contained unreacted $W_2(NMe_2)_6$. The pink powder is air-stable, insoluble in all common solvents and non-volatile. On heating in vacuo dimethylamine hydrochloride sublimes leaving a darkened residue. Analytical data and infrared data for the pink powder are recorded in the experimental section.

$M_2(NMe_2)_6$ + Me_3SiCl. Hydrocarbon solutions of $M_2(NMe_2)_6$ (M = Mo and W) react smoothly with Me_3SiCl (2 equiv) at room temperature according to eq. 1.

$$\underset{\sim}{1} \quad M_2(NMe_2)_6 + 2Me_3SiCl \longrightarrow M_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2$$

The reaction is quantitative. Me_3SiNMe_2 is very volatile and may be removed in vacuo along with the solvent, thus leaving the less volatile $M_2Cl_2(NMe_2)_4$ compounds. The latter may be purified by vacuum sublimation (100-120°C, 10^{-4} cm Hg) and by crystallization from hexane or toluene.

Reaction 1 was followed by nmr spectroscopy and was seen to proceed rapidly ($t_\infty \sim 30$ min at 40°) and stereospecifically: only anti $M_2Cl_2(NMe_2)_4$ compounds are formed in nmr detectable concentrations.

The reactions of $W_2(NMe_2)_6$ and Me_3SiCl (x equiv) in benzene have also been studied but compounds $W_2Cl_x(NMe_2)_{6-x}$ have been isolated only for X = 2. With 1 equivalent of Me_3SiCl an equilibrium mixture of $W_2(NMe_2)_6$, $W_2Cl(NMe)_5$ and

$W_2Cl_2(NMe_2)_4$, eq. 2, is formed in solution, but upon crystallization only $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ were isolated

$$\underset{\sim}{2} \qquad W_2Cl_2(NMe_2)_4 + W_2(NMe_2)_6 \rightleftarrows 2W_2Cl(NMe_2)_5 \qquad K \simeq 1 \text{ at } 30^\circ C$$

The equilibrium 2 is rapidly attained upon dissolving mixtures of $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$.

Although ^1H nmr studies (see later) suggest the existence of compounds $W_2Cl_x(NMe_2)_{6-x}$, where $x > 2$, none have been isolated from solution. A reaction between $W_2Cl_2(NMe_2)_4$ and Me_2SiCl (2 equiv) in benzene was followed by ^1H nmr spectroscopy. Formation of Me_3SiNMe_2 was apparent but the only isolable tungsten species were a black insoluble non-volatile solid and $W_2Cl_2(NMe_2)_4$. Thus, although a number of compounds of general formula $W_2Cl_x(NMe_2)_{6-x}$ may exist in equilibrium with each other in solution, it appears that only $W_2Cl_2(NMe_2)_4$ and $W_2(NMe_2)_6$ are readily isolable from such systems. The formation of a black insoluble, non-volatile compound in the reaction between $W_2(NMe_2)_6$ and Me_3SiCl (4 equiv) leads us to believe that a polymeric structure is adopted as x tends to 6.

Mechanisms

A number of reasons lead us to propose the amine catalyzed reaction sequence 3 for the chloro-for-dimethylamide exchange reactions described above: (1) The equilibrium

$$\underset{\sim}{3} \qquad \text{(i)} \quad Me_3SiCl + HNMe_2 \rightleftarrows Me_3SiNMe_2 + HCl$$

$$\text{(ii)} \quad L_nW\text{-}NMe_2 + HCl \rightleftarrows L_nW\text{-}Cl + HNMe_2$$

3(i) is well documented.[16] (2) Hydrocarbon solutions of $M(NMe_2)n$ compounds invariably contain trace quantities of amine and this

has been shown[17] to be responsible for the amine catalyzed insertion of CO_2 into M-NMe_2 bonds: $CO_2 + HNMe_2 \rightleftarrows HO_2CNMe_2$; M-$NMe_2$ + $HO_2CNMe_2 \rightarrow MO_2CNMe_2 + HNMe_2$. (3) when Me_3SiCl (3 equiv) was added to a hydrocarbon solution of $W_2(NMe_2)_6$ and $LiBu^t$ (1 equiv) no reaction involving $W_2(NMe_2)_6$ occurred over a period of 4 hr. Subsequent addition of $HNMe_2$ initiated the reaction leading to $W_2Cl_2(NMe_2)_4$. (4) Addition of $HN(CD_3)_2$ (4 equiv) to a benzene solution of $W_2(NMe_2)_4Cl_2$ led to the virtually instantaneous formation of $W_2(NMe_2)_6$ and some pink solid. Significantly the integral ratio of W-NMe_2 to $HNMe_2$ methyl protons was 1:1. Since $W_2(NMe_2)_6$ and $HN(CD_3)_2$ do not react under comparable conditions[17] the observed $HNMe_2/HN(CD_3)_2$ scrambling and the formation of $W_2(NMe_2)_6$ support the facile equilibrium 3(ii). It should also be noted that the facile equilibrium 3(ii) can readily account for the rapid establishment of the equilibrium 2 which is attained on mixing $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ in solution and for our inability to isolate $W_2Cl(NMe_2)_5$ from such solutions.

<u>$M_2Cl_2(NMe_2)_4$</u>. $M_2Cl_2(NMe_2)_4$, where M = Mo and W, are yellow, crystalline, extremely air-sensitive solids. They are volatile and may be sublimed <u>in vacuo</u> at 100-120°, 10^{-4} cm Hg. They show strong molecular ions in the mass spectrometer, $M_2Cl_2(NMe_2)_4^+$, together with other dinuclear ions such as $M_2Cl(NMe_2)_4^+$, $M_2Cl_2(NMe_2)_3^+$ and $M_2Cl_2(NMe_2)_2^+$. They are soluble in hydrocarbon solvents but are decomposed in ether and tetrahydrofuran. Infrared data are recorded in the experimental section.

<u>Solid State Structures</u>. The positional and thermal vibrational parameters for the molybdenum and tungsten compounds are listed in Tables 1 and 2, respectively. The two compounds are isostructural. Figure 1 shows one of the two molecules of the tungsten compound and defines the numbering scheme for the atoms in that molecule.

For the molybdenum compound the numbering scheme is directly analogous. For both compounds there are two crystallographically independent but virtually identical molecules in the unit cell, each having a crystallographically rigorous center of inversion. All intermolecular contacts are normal. Bond distances and bond angles for both compounds are listed in Table 3.

The structures are the expected ones: in each a set of six groups is attached to a central M_2 moiety in a staggered ethane-like configuration with an anti rotational conformation. This, together with the observed diamagnetism of the compounds and the short M-M distances (2.201(2)Å, M = Mo; 2.285(2)Å, M = W) which are ca. 1.0Å shorter than the M-M single bonds in $Cp_2M_2(CO)_6$,[18] forms the basis for our claim that there exist metal-to-metal triple bonds.

The planarity of the $M-NC_2$ moieties and the short M-N bond distances are indicative of N-to-M π-bonding. The M-N distances in $M_2Cl_2(NMe_2)_4$ are ca. 0.04Å shorter than in the related parent compounds $M_2(NMe_2)_6$,[6,7] which is not unexpected. Substitution of the more electronegative and less π-donating Cl ligand would be expected to increase N-to-M π-bonding in the remaining $M-NMe_2$ groups.

The M-M distances for a series of M_2L_6 and $M_2X_2L_6$ compounds are given in Table 4. All these compounds adopt the staggered ethane-like geometry. The M-M distances vary only slightly, 2.167 to 2.300Å, but, in view of the accuracy to which the M-M distance is known, these differences may be deemed significant and as such are worthy of comment. (1) The W-W bond distances are ca. 0.08Å longer than the Mo-Mo distances in related pairs of molecules. This would correspond to a difference of 0.04Å

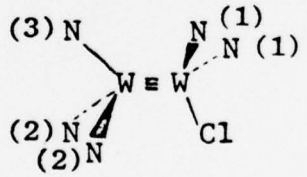
in the metal triple-bond radii, W > Mo. No significant difference exists between the W-Cl and Mo-Cl bond lengths, nor, within the very large esd's, between the W-N and Mo-N distances. The difference in the Mo-Mo and W-W distances may reflect the presence of filled 4f shells in the W atoms which may create a repulsive force that is significant in the short W-W bond but not in the W-ligand bonds where only one such filled inner shell is present. (2) Within a given series M_2L_6, where L = R(alkyl), NR_2 or OR, the M-M distances follow the order $NR_2 \sim OR > R$, which suggests that the π-donating ligands (OR and NR_2) cause a significant increase in M-M distance. Of course steric factors may also contribute to M-M bond distances. However, the steric demand of the OCH_2CMe_3 ligand must be less than the CH_2SiMe_3 ligand and yet the M-M distance in the latter is 0.06Å shorter than the former. Similarly comparing the M-M distances in $M_2(NMe_2)_6$ and $M_2Cl_2(NMe_2)_4$ shows that substitution of Cl for NMe_2 is accompanied by a small decrease in M-M distance. (3) The differences in W-W bond distances in $W_2Cl_2(NMe_2)_4$ (2.285Å) and $W_2Cl_2(NEt_2)_4$ (2.301Å) is 0.016Å which is about five times the esd and as such is considered to be real. All the other bonding parameters are essentially identical for these two molecules and so it seems that this change in W-W distance may also be attributed to the electron releasing properties of the ligand $NEt_2 > NMe_2$.

<u>^{1}H NMR Spectra</u>. Variable temperature ^{1}H nmr spectra of $M_2Cl_2(NMe_2)_4$ were recorded in toluene-d_8 in the temperature range $+90^0$ to -90^0C. At high temperatures a single methyl resonance was observed which on cooling broadened, collapsed into the base-line and then at low temperatures led to a two-line spectrum in the integral ratio 1:1. These observations are consistent with existence of only the anti-rotamer in solution and correspond to the temperature dependent rate of

proximal-distal alkyl exchange.[6] From the coalescence temperature we estimate the free energies of activation for proximal-distal exchange to be 16.0 (Mo) and 13.9(W) kcal $mole^{-1}$. These values are significantly higher than those for $M_2(NMe_2)_6$ compounds, $\Delta G^{\ddagger}$ = 11.5 (Mo), 11.2 kcal mol^{-1} (W), which probably reflects the greater degree of N-to-M π-bonding in $M_2Cl_2(NMe_2)_4$ compounds.

<u>$W_2Cl(NMe_2)_5$</u>. Our evidence for the existence of this compound is based primarily upon ^1H nmr studies. All attempts to isolate crystals of $W_2Cl(NMe_2)_5$ from solutions of equilibrium mixtures 2 yielded $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$: however, the ion $W_2Cl(NMe_2)_5^+$ was observed in the mass spectrum of solids obtained from stripping the solvent of equilibrium mixtures 2.

Since both $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ adopt a staggered ethane-like geometry we assume that $W_2Cl(NMe_2)_5$ will adopt the ground state geometry shown below



Note there are three types of dimethylamido groups: N(1), N(2) and N(3). From our knowledge of the dynamical solution behavior of other compounds of the type $W_2X_2(NR_2)_4$[11,13] we can anticipate the variable temperature ^1H nmr spectra for $W_2Cl(NMe_2)_5$. A low temperature limiting spectrum should consist of two well separated sets of 3 line resonances corresponding to frozen out proximal and distal methyl groups of the three types of NMe_2 ligands. Each three line pattern should be in the integral ratio 2:2:1. On raising the temperature we expect a pair-wise collapse of these resonances to give a 3 line spectrum in the

integral ratio 4:4:2 corresponding to rapid proximal-distal exchange. If anti ⇄ gauche isomerization became fast on the nmr time scale two situations might be realized: (1) a two line spectrum of integral intensity 6:4 or (2) a single resonance. The former would correspond to rapid rotation about the W-W bond as in ethane, while the latter would arise from rapid NMe_2 group transfer between the two tungsten atoms. This might be achieved by either an intramolecular (cf.[20] M-CO scrambling in bimetallic and polynuclear metal carbonyls) or an intermolecular mechanism e.g. by amine catalysis.

With these considerations in mind we obtained variable temperature ^1H nmr spectra of various equilibrium mixtures of $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ in the temperature range $+125^0$ to -90^0C at 60, 100 and 270 MHz. These spectra are consistent with our expectations of the dynamical solution behavior of $W_2Cl(NMe_2)_5$ although the presence of $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ leads to degeneracies of some of the resonances at certain temperatures.

At 100^0C in toluene-d_8 at 100 MHz a three line spectrum is observed. The low field resonance is readily assigned to the methyl resonances of $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$ which are accidentally magnetically degenerate. The two lower field resonances are in the integral ratio 2:1 and are assigned to two of the three types of NMe_2 groups of $W_2Cl(NMe_2)_5$. We conclude: (1) At this temperature proximal-distal methyl exchange is fast on the nmr time scale for all three compounds $W_2Cl_x(NMe_2)_{6-x}$, where x = 0,1 and 2. (2) For $W_2Cl(NMe_2)_5$ one pair of NMe_2 methyl resonances must be accidentally degenerate with the methyl resonances of $W_2(NMe_2)_6$ and $W_2Cl_2(NMe_2)_4$. (3) Rotation about the W≡W bond in $W_2Cl(NMe_2)_5$ must be slow on the nmr time scale

at this temperature and (4) the equilibrium reaction 2 is slow on the nmr time scale at this temperature. If this were not so we would observe a single resonance for all the species present in solution.

On lowering the temperature five processes are observed. These are, in decreasing order of free energy of activation, proximal-distal methyl exchange for (i) anti-$W_2Cl_2(NMe_2)_4$ (ii) the N(1) groups in $W_2Cl(NMe_2)_5$ (iii) $W_2(NMe_2)_6$ (iv) the NMe_2 group anti-to-Cl in $W_2Cl(NMe_2)_5$, N(1), and (v) the N(2) groups in $W_2Cl(NMe_2)_5$.

An absolute assignment of N(1) and N(2) groups in $W_2Cl(NMe_2)_5$ is not possible. We believe the above assignment to be the more reasonable from steric and electronic considerations.

The free energies of activation for proximal-distal methyl exchange for $W_2(NMe_2)_6$ and for the N(3) group in $W_2Cl(NMe_2)_5$ are virtually identical. This presumably reflects the very similar environments of the NMe_2 groups in both molecules.

Experimental Section

Materials. Dimetaldialkylamides, $M_2(NMe_2)_6$ (M = Mo[6],W[7]) were prepared according to published procedures. $ClSiMe_3$ was purchased from Aldrich.

General Procedures. All manipulations were carried out in an atmosphere of dry and oxygen free nitrogen. All solvents were distilled from a Na-K alloy immediately before use or stored over CaH_2 in a N_2 atmosphere until used. $(CH_3)_3SiCl$ was stored over molecular sieves, then distilled and stored under N_2. It was usually measured (ca. 2% accuracy) on a calibrated vacuum manifold, then condensed into the reaction flask with liquid N_2.

Physical and Analytical Measurements. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using dry box sampling techniques. Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer 283 spectrophotometer.

^1H NMR spectra were obtained from 60, 100 and 270 MHz instruments equipped with variable temperature probes. Mass spectra were obtained using an AEI MS9 mass spectrometer and the method of direct insertion (80-120°C) was used.

Preparation of $M_2Cl_2(NMe_2)_4$ (M = W,Mo). In a typical experiment $ClSiMe_3$ (7.4 mmole) were added to a frozen solution of $M_2(NMe_2)_6$ (3.6 mmole) in toluene (40 ml). After stirring the solution at ca. 40°C for 24 hr., the color changed gradually from yellow to red. The solvent, along with the Me_2NSiMe_3 was removed by vacuum. The orange-yellow compound was then sublimed at 110°C (10^{-4} mmHg) and/or recrystallized from toluene. Typical yields ranged from 80 to 90%. The reaction may be carried out at room temperature but sometimes it may take several days to go to completion. Anal. Calcd. for $Mo_2Cl_2(NMe_2)_4$: C, 21.88;

H, 5.51; N, 12.76; Cl 16.15. Found: C, 22.05; H, 5.43, N, 12.64; Cl, 16.07. Anal. Calcd. for $W_2Cl_2(NMe_2)_4$: C, 15.63; H, 3.93; N, 9.11; Cl, 11.53. Found: C, 15.86; H, 3.98; N, 8.92; Cl, 11.68. Infrared absorptions of $Mo_2Cl_2(NMe_2)_4$ (cm^{-1}): 2770(w), 1418(w), 1412(w), 1260(w), 1238(w), 1140(m), 1038(m), 1030(w), 945 (vs), 934(vs), 800(m), 570(s), 374(s), 348(w), 310(w); $W_2Cl_2(NMe_2)_4$: 2775(w), 1422(w), 1260(w), 1245(s), 1145(s), 1039(m), 1032(m), 952(vs), 938(vs), 803(w), 565(s), 360(s), 319(w).

Reaction of $W_2(NMe_2)_6$ + HCl. HCl (3.90 mmole) was added to a frozen solution of $W_2(NMe_2)_6$ (1.95 mmole) in toluene (40 ml). As soon as the solution melted, there was change in color from yellow to pale red. The solution was allowed to warm to room temperature slowly and then stirring was continued for 3 hours. By then there was a pink precipitate and a red-brown solution. The precipitate was filtered and washed with hexane. The filtrate was dried giving a sticky black solid which contains $W_2(NMe_2)_6$ and small amounts of $W_2Cl_2(NMe_2)_4$. The pink precipitate is virtually insoluble in most common organic solvents and appears to be stable to air and moisture. Infrared absorptions of pink precipitate (cm^{-1}): 3200(m), 2455(m), 1419(w), 1410(w), 1250(s), 1148(m), 1052(m), 1040(vs), 1008(s), 938(vs), 888(s), 795(m), 572(w), 394(w), 303(s), 278(m), 258(m).

Reaction of $W_2Cl_2(NMe_2)_4$ + $2Me_3SiCl$. Me_3SiCl (0.882 mmole) was added to a frozen solution of $W_2Cl_2(NMe_2)_4$ (0.441 mmole) in toluene (20 ml) in an ampoule, which was then sealed. After 8 days at room temperature, there was a black precipitate and a red-brown solution. The ampoule was opened in a dry box and its entire contents were put into a flask and filtered. The solvent was then removed under vacuum from the solution. There was a mixture of compounds; a black solid which gave an infrared

spectrum similar to the precipitate, a pink compound similar to that formed in the reaction above, and a small amount of $W_2Cl_2(NMe_2)_4$. Infrared data for the black precipitate after washing with toluene: (cm^{-1}): 1305(w), 1260(s), 1145(w), 1090 (b,s), 950(w), 938(s), 890(w), 800(b,s), 568(s), 392(m), 360(m), 308(m).

Reaction of $W_2(NMe_2)_6 + 3Me_3SiCl + LiBu^t$. Me_3SiCl (2.53 mmole) was added to a frozen solution of $W_2(NMe_2)_6$ (0.85 mmole) and $LiBu^t$ (0.85 mmole) in hexane (15 ml). The reaction mixture was stirred and allowed to quickly reach room temperature. After several hours there was no evidence that a reaction was occuring. The reaction mixture was then frozen and a trace of $HNMe_2$ was added. When the solution melted and returned to room temperature the color changed quickly to red brown, with the appearance of a yellow-green precipitate. The mixture was stirred overnight and the precipitate was filtered and washed with two 4 ml portions of cool hexane. $W_2Cl_2(NMe_2)_4$ was identified by ^1H nmr spectroscopy and by i.r. spectroscopy.

Reaction of $W_2Cl_2(NMe_2)_4 + HNMe_2\text{-}d_6$. $W_2Cl_2(NMe_2)_4$ (0.093 mmole) were placed in an NMR tube and dissolved in toluene-d_8. To this, 4 equivalents of $HNMe_2\text{-}d_6$ (0.37 mmole) were added to the frozen solution and the tube was then sealed. Upon melting, the color changed from yellow to dark brown. Some red and brown precipitates also appeared. ^1H NMR spectra showed that $W_2(NMe_2)_4$ is formed along with the appearance of $HNMe_2$ in a ratio of 1:1.

Crystal Data and Structure Determination for $W_2Cl_2(NMe_2)_4$. A large yellow crystal was ground to a sphere with a diameter of 0.56 mm and mounted in a glass capillary under argon. Several attempts to grind crystals to smaller spheres resulted in crumbling of the crystal. The crystal was then examined on a Syntex $P\bar{1}$ four-circle automated diffractometer. The ω and $\theta/2\theta$ scans were slightly unsymmetrical for some reflections but

rotation photographs suggested that the crystal was of acceptable quality for data collection. At small scattering angles the peak widths at half-height were $\leq 0.25^0$.

For the calculation of lattice parameters, fifteen of the strongest reflections in the range $20^0 < 2\theta(\text{MoK}\alpha) < 31^0$ were selected to give a variety of crystal orientations using the angular settings for these reflections, the following lattice parameters were obtained from the Syntex software package (MoKα λ = 0.71073Å): a = 15.061(8)Å, b = 13.338(7)Å, c = 8.372(3)Å, β = 96.68(3)^0, and V = 1670(1)Å^3. For the monoclinic space group $P2_1/c$ with Z = 4, and a molecular weight of 614.9 Daltons, the calculated density is 2.445 gcm^{-3}.

Intensity data were collected at 23±1^0 using graphite-monochromatized MoKα radiation and θ-2θ scan rates varying from 4 to 24^0/min, depending on the intensity of the reflection. Background measurements were made at both limits of each scan. Of the 3432 integrated intensities collected in the range $0^0 < 2\theta\ (\text{MoK}\alpha) < 53^0$, 2077 unique observations with $I > 3\sigma(I)$ were retained as observed data and corrected for Lorentz and polarization effects. Three standard reflections remeasured after every 50 data points showed a small linear decomposition, for which appropriate correction was made to the experimental structure factors. Since the linear absorption coefficient is 148.8 cm^{-1} a spherical absorption correction was applied. The average transmission is 1.9% with the high and low transmissions being 2.6% and 1.0%, respectively. It is obvious that the use of such a large crystal in a compound with a large linear absorption coefficient is a disadvantage, but as already noted, smaller spheres could not be obtained and the use of a small non-spherical crystal would be undesirable because of the effect of errors in the measurement of crystal dimensions.

A three dimensional Patterson map revealed the positions of two tungsten atoms belonging to two independent molecules each placed at one of the inversion centers at 0, 0, 0 and 1/2, 0, 1/2. The same result was obtained from a solution using direct methods.[21] A difference Fourier map based on the refined position of the tungsten atoms revealed all but two of the non-hydrogen atoms. The remaining atoms were found on successive cycles of refinement and difference Fourier maps. Refinement was carried out with isotropic and then with anisotropic thermal parameters on all non-hydrogen atoms to final discrepancy indices

$$R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o| = 0.072$$

and

$$R_2 = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2} = 0.088$$

The error in an observation of unit weight was 1.9. No attempt was made to locate and refine hydrogen atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $p = 0.06$ was used in the previously defined expression for the weights.[22,23] The scattering factor tables were from reference 24. Corrections for anomalous scattering by the tungsten atoms were taken from Cromer and Liberman.[25]

A final difference map contained some peaks with relatively high electron density around the tungsten atoms. Most of these peaks were to close to the tungsten atoms to be of any chemical significance. The peaks are readily understood to reflect the inadequacy of the simple decomposition correction and the high absorption correction applied to the intensity data. No unusual trends were observed in an analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of reflection number, $\lambda^{-1} \sin \theta$, or various classes of indices.

A list of observed and calculated structure factors is available.[26]

Data and Structure Refinement for $Mo_2Cl_2(NMe_2)_4$. An approximately bipyramidal, yellowish crystal measuring ca. 0.2 x 0.2 x 0.3 mm was mounted in a capillary under nitrogen. The crystal was shown to be of good quality from ω-scans of several intense reflections which had peak widths at half-height of less than 0.2^0. Preliminary lattice constants suggested that $Mo_2Cl_2(NMe_2)_4$ was isostructural with the previously examined $W_2Cl_2(NMe_2)_4$. The final lattice parameters were calculated from 15 strong reflections in the range $20.0^0 < 2\theta(MoK\alpha) < 25.0^0$, chosen to give a good sampling of crystal indices. Final lattice parameters are: a = 15.031(2)Å, b = 13.246(1)Å, c = 8.411(1)Å, β = 96.36(1)^0, and V = 1664.3(3)Å^3.

Data collection was carried out as described for $W_2Cl_2(NMe_2)_4$. The integrated intensities of 2522 reflections having $0^0 < 2\theta MoK\alpha < 45.6^0$ were measured. Three standard reflections, remeasured after every 97 data points, indicated that very slow decomposition was occurring, and an appropriate correction was made to the experimental structure factors. The average correction was 6.9%, and the maximum correction was 12.2%. 2294 unique reflections of which 1655 had $I > 3\sigma(I)$ were retained and corrected for Lorentz and polarization effects. The linear absorption coefficient of $Mo_2Cl_2(NMe_2)_4$ is 17.8 cm^{-1}; an absorption correction was not applied to the data.

The weighting scheme and the discrepancy values, R_1 and R_2, have been described above. 1655 reflections having $I > 3\sigma(I)$ were used in the structure refinement. Initial positions for the 16 atoms were taken from the $W_2Cl_2(NMe_2)_4$ structure. The positional and isotropic thermal parameters were refined to R_1 = 0.059 and R_2 = 0.084. Anisotropic thermal parameters were then introduced for the Mo and Cl atoms and refinement was continued until it

converged with the following discrepancy indices; $R_1 = 0.046$ and $R_2 = 0.069$. The error in an observation of unit weight was 1.45. During the final cycle of refinement no parameter shifted by more than 0.01σ. A final difference Fourier map revealed no significant features. A table of observed and calculated structure factor amplitudes is available.[26]

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Supplementary Material Available. Listings of the structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Table 1. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2Cl_2(NMe_2)_4$

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.44791(6)	0.05511(7)	0.4578(1)	0.00243(4)	0.00293(5)	0.0090(1)	0.00082(8)	0.0010(1)	0.0009(2)
Mo(2)	-0.03081(6)	0.07150(7)	0.0321(1)	0.00265(4)	0.00311(5)	0.0098(1)	-0.00089(9)	0.0014(1)	-0.0013(2)
CL(1)	0.3903(2)	0.0068(3)	0.1974(4)	0.0046(2)	0.0078(2)	0.0102(4)	-0.0013(4)	-0.0021(5)	-0.0004(6)
CL(2)	-0.0913(2)	0.0427(3)	0.2731(4)	0.0047(2)	0.0072(2)	0.0130(5)	-0.0010(3)	0.0054(5)	-0.0009(6)
				$B(Å)^2$					
N(1)	0.3637(6)	0.0394(7)	0.614(1)	2.6(2)					
N(2)	0.5122(6)	0.1818(8)	0.470(1)	3.4(2)					
N(3)	0.0700(6)	0.1640(8)	0.048(1)	3.3(2)					
N(4)	-0.1194(6)	0.0939(7)	-0.147(1)	3.1(2)					
C(1)	0.3618(9)	-0.019(1)	0.761(2)	3.8(3)					
C(2)	0.2867(9)	0.112(1)	0.596(2)	4.0(3)					
C(3)	0.6042(9)	0.209(1)	0.533(2)	4.7(3)					
C(4)	0.4542(10)	0.271(1)	0.426(2)	5.2(3)					
C(5)	0.1649(9)	0.155(1)	0.025(2)	4.3(3)					
C(6)	0.0456(10)	0.272(1)	0.070(2)	5.1(3)					
C(7)	-0.1423(9)	0.042(1)	-0.302(2)	4.1(3)					
C(8)	-0.1765(9)	0.185(1)	-0.138(2)	4.8(3)					

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Table 2. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2Cl_2(NMe_2)_4$

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.44536(7)	0.05566(8)	0.4539(1)	0.00264(4)	0.00419(5)	0.0108(1)	0.00094(9)	0.0035(1)	0.0009(2)
W(2)	-0.03138(7)	0.07344(8)	0.0360(1)	0.00290(4)	0.00416(5)	0.0133(1)	-0.00103(9)	0.0046(1)	-0.0014(2)
CL(1)	0.3909(5)	0.0055(7)	0.1941(10)	0.0048(4)	0.0085(6)	0.014(1)	-0.0015(8)	0.002(1)	0.001(1)
CL(2)	-0.0882(5)	0.0424(7)	0.2780(9)	0.0055(4)	0.0090(6)	0.015(1)	-0.0018(8)	0.009(1)	-0.002(1)
N(1)	0.363(1)	0.044(2)	0.615(2)	0.0040(10)	0.005(1)	0.005(2)	0.000(2)	-0.001(3)	-0.001(3)
N(2)	0.507(2)	0.182(2)	0.464(3)	0.0032(10)	0.008(2)	0.014(4)	-0.003(2)	-0.002(4)	0.008(4)
N(3)	0.070(1)	0.168(2)	0.048(3)	0.0023(9)	0.005(1)	0.022(4)	0.000(2)	0.005(3)	0.002(4)
N(4)	-0.122(1)	0.099(2)	-0.141(3)	0.0024(9)	0.006(1)	0.019(4)	0.004(2)	-0.005(4)	0.001(4)
C(1)	0.359(2)	-0.018(3)	0.756(4)	0.006(1)	0.012(3)	0.014(4)	-0.008(3)	0.011(4)	-0.003(6)
C(2)	0.284(2)	0.112(3)	0.586(5)	0.003(1)	0.006(2)	0.037(8)	0.000(3)	0.004(6)	-0.010(7)
C(3)	0.601(2)	0.211(2)	0.522(5)	0.005(1)	0.007(2)	0.026(7)	-0.007(3)	0.004(5)	0.001(6)
C(4)	0.450(3)	0.274(2)	0.431(4)	0.009(2)	0.006(2)	0.027(6)	0.006(3)	0.012(6)	0.017(5)
C(5)	0.162(2)	0.160(3)	0.021(5)	0.002(1)	0.010(2)	0.033(8)	-0.003(3)	0.001(5)	-0.017(7)
C(6)	0.047(2)	0.272(2)	0.082(4)	0.006(2)	0.004(2)	0.026(7)	-0.004(3)	0.005(6)	-0.017(7)
C(7)	-0.147(2)	0.050(3)	-0.294(5)	0.003(1)	0.012(3)	0.022(6)	-0.004(4)	0.001(5)	0.001(8)
C(8)	-0.176(2)	0.189(3)	-0.125(5)	0.004(1)	0.006(2)	0.034(8)	0.004(3)	0.001(6)	0.007(7)

The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Table 3. Bond Distances (Å) and Angles (deg) in $Mo_2Cl_2(NMe_2)_4$ and $W_2Cl_2(NMe_2)_4$.[a-c]

Atoms / Bonds	$Mo_2Cl_2(NMe_2)_4$		$W_2Cl_2(NMe_2)_4$	
	Molecule I	Molecule II	Molecule I	Molecule II
M(1)-M(1)'	2.200(2)	2.202(2)	2.283(2)	2.287(2)
M(1)-Cl(1)	2.353(3)	2.343(3)	2.332(6)	2.326(6)
M(1)-N(1)	1.94(1)	1.94(1)	1.94(1)	1.97(2)
M(1)-N(2)	1.93(1)	1.92(1)	1.92(2)	1.93(2)
N(1)-C(1)	1.45(1)	1.47(1)	1.46(3)	1.44(3)
N(1)-C(2)	1.50(1)	1.49(1)	1.49(3)	1.47(3)
N(2)-C(3)	1.47(1)	1.47(1)	1.49(3)	1.45(3)
N(2)-C(4)	1.50(1)	1.49(1)	1.50(3)	1.46(3)
Angles				
M(1)'-M(1)-Cl(1)	107.2(1)	106.7(1)	106.9(2)	106.4(2)
-N(1)	101.8(2)	102.4(3)	102.0(5)	102.6(5)
-N(2)	103.0(3)	102.3(3)	103.3(6)	103.1(6)
Cl(1)-M(1)-N(1)	113.8(2)	114.6(3)	116.3(5)	115.4(6)
-N(2)	114.7(3)	113.8(3)	114.1(6)	113.8(6)
N(1)-M(1)-N(2)	114.6(3)	115.2(4)	112.4(7)	113.6(8)
M(1)-N(1)-C(1)	135.1(7)	134.8(7)	134(2)	135(2)
-C(2)	114.5(6)	114.4(7)	114(1)	115(1)
M(1)-N(2)-C(3)	132.6(7)	134.0(7)	133(2)	134(2)
-C(4)	113.7(7)	115.8(7)	117(1)	115(2)
C(1)-N(1)-C(2)	109.9(8)	110.3(9)	112(2)	110(2)
C(3)-N(2)-C(4)	113.3(9)	110.2(9)	110(2)	111(2)

[a] Numbers in parenthesis are the estimated standard deviations in the last significant digit.

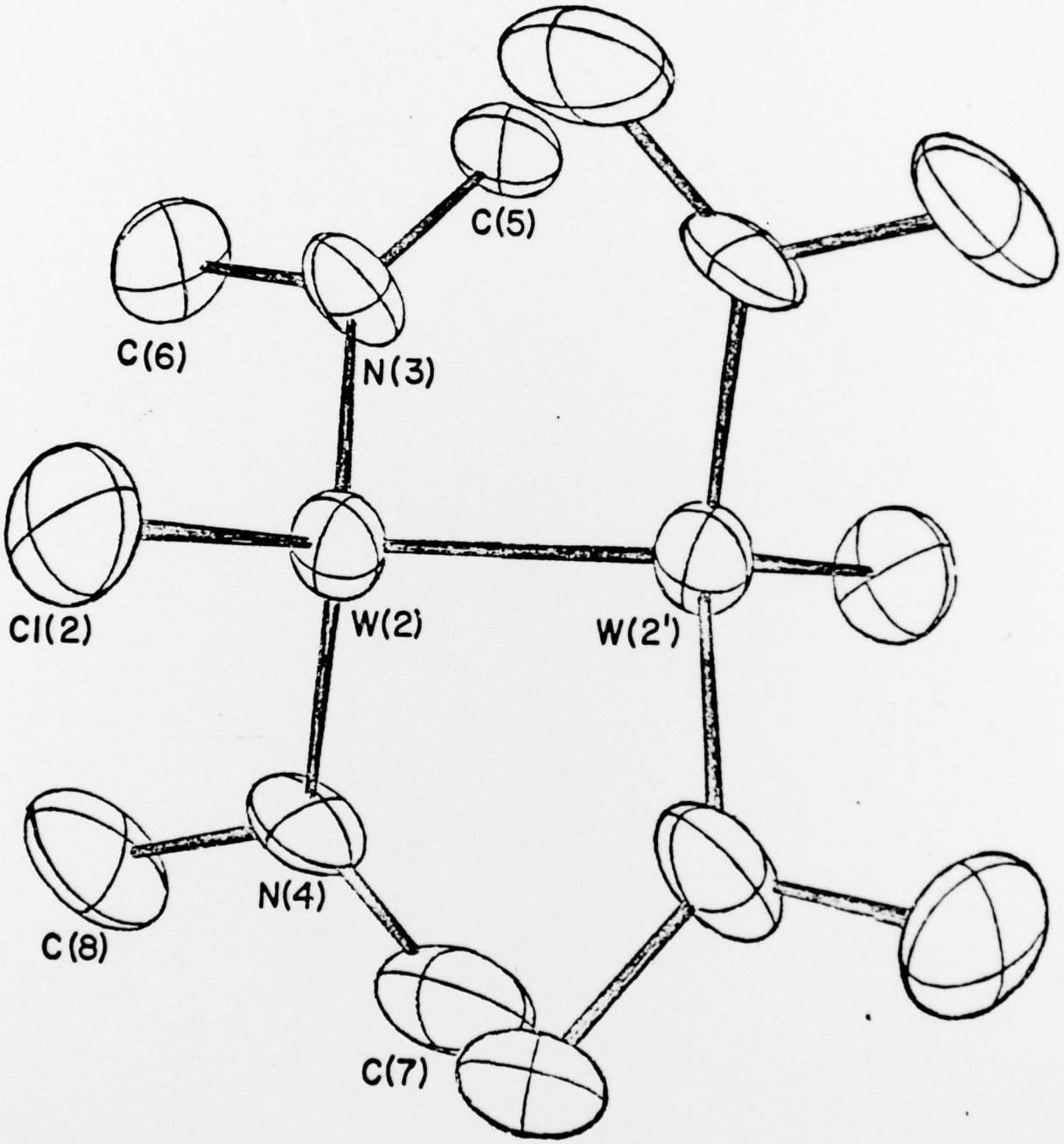
[b] Atoms of molecule II are labeled as in Figure 1 ; to obtain the proper labels for the atoms in molecule I substitute M(1), Cl(1), N(1), N(2), C(1), C(2), C(3), and C(4) for M(2), Cl(2), N(3), N(4), C(5), C(6), C(7), and C(8), respectively.

[c] Primed atoms are related by a center of symmetry to the corresponding unprimed atoms.

Table 4. M-M Triple Bond Distances in M_2L_6 and $M_2X_2L_4$ Compounds

Compounds	M-M Å	ref.
$Mo_2(CH_2SiMe_3)_6$	2.167(?)	3
$W_2(CH_2SiMe_3)_6$	2.255(2)	5
$Mo_2(NMe_2)_6$	2.214(3)	6
$W_2(NMe_2)_6$	2.294(2)	7
$Mo_2(OCH_2CMe_3)_6$	2.222(2)	8
$Mo_2Cl_2(NMe_2)_4$	2.201(2)	this work
$W_2Cl_2(NMe_2)_4$	2.285(2)	this work
$W_2Cl_2(NEt_2)_4$	2.301(1)	11
$W_2Br_2(NEt_2)_4$	2.301(2)	12
$W_2I_2(NEt_2)_4$	2.300(4)	12
$W_2Me_2(NEt_2)_4$	2.291(1)	13

Figure 1. An ORTEP perspective view of one of the $W_2Cl_2(NMe_2)_4$ molecules. The atoms are represented by 50% probability thermal ellipsoids.


C(5)
C(6)
N(3)
Cl(2)
W(2)
W(2')
N(4)
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